

FORM PTO-1390  
(REV. 11-2000)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

069918.000002

U S APPLICATION NO (if known, see 37 CFR 1.5)

Unknown

09/889282

INTERNATIONAL APPLICATION NO.  
PCT/GB00/00062 ✓INTERNATIONAL FILING DATE  
12 January 2000 ✓

PRIORITY DATE CLAIMED

14 January 1999 ✓

TITLE OF INVENTION

\*RETROREFLECTIVE INKS ✓

APPLICANT(S) FOR DO/EO/US

Brian Sagar ✓

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: return postcard ; Small Entity Statement (2)

U.S. APPLICATION NO. of known PCT/US  
 09/889282

INTERNATIONAL APPLICATION NO  
 PCT/GB00/00062

ATTORNEY'S DOCKET NUMBER  
 069918.000002

21. ☒ The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)  
 nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
 and International Search Report not prepared by the EPO or JPO..... **\$1000.00**

International preliminary examination fee (37 CFR 1.482) not paid to  
 USPTO but International Search Report prepared by the EPO or JPO ..... **\$860.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
 but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
 but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **\$690.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
 and all claims satisfied provisions of PCT Article 33(1)-(4) ..... **\$100.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

**CALCULATIONS PTO USE ONLY**

\$ 860

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30  
 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	56 - 20 =	36	x <b>\$18.00</b>	\$ 648	
Independent claims	5 - 3 =	2	x <b>\$80.00</b>	\$ 160	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ <b>\$270.00</b>	\$	

**TOTAL OF ABOVE CALCULATIONS =** \$1648

☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above  
 are reduced by 1/2.

+

\$

**SUBTOTAL =** \$ 824

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30  
 months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

**TOTAL NATIONAL FEE =** \$ 824

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
 accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

\$ 40

**TOTAL FEES ENCLOSED =** \$ 864

Amount to be  
 refunded:

\$

charged:

\$

a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 50-0259 in the amount of \$ 864 to cover the above fees.  
 A duplicate copy of this sheet is enclosed. (069918.000002)

c. ☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
 overpayment to Deposit Account No. \_\_\_\_\_. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card  
 information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO

James E. Bradley  
 Bracewell & Patterson, L.L.P.  
 P.O. Box 61389  
 Houston, Texas 77208-1389  
 (713) 223-2900

SIGNATURE

James E. Bradley

NAME

27,536

REGISTRATION NUMBER

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

**Brian Sagar**

SERIAL NO: **Unknown**

FILED: **Herewith**

TITLE: **Retroreflective Inks**

§  
§  
§  
§  
§  
§  
§  
§

DOCKET NO.: **069918.000002**

GROUP ART NO.: **Unknown**

EXAMINER: **Unknown**

**PRELIMINARY AMENDMENT**

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

Sir:

Please amend the above-identified application as follows:

Cancel claims 1-56.

Add new claims 57-113 as set forth below.

57. <sup>4</sup> A combination of ingredients, especially for use in the formulation of a one or two-pack retroreflective ink, comprising retroreflective elements, microbeads additional to said retroreflective elements or constituting said retroreflective elements at least in part, binder chemicals for attaching the retroreflective elements and microbeads to a substrate to which the ink is to be applied, and a coupling agent for coupling the microbeads and cross-linking the binder chemicals, the coupling agent being unreactive until the printing process is carried out.

58. The combination of claim 57 wherein the coupling agent is unreactive except at elevated temperature at which the substrate is printed and cured.

59. The combination of claim 57 wherein at least some of the microbeads are without the retroreflective elements.

60. The combination of claim 57 wherein the binder chemical and the coupling agent are selected from the group consisting of:

a polyvinylidene chloride copolymer is the binder chemical and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer is the coupling agent,

an acrylic copolymer is the binder chemical and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer is the coupling agent, and

a polyurethane is the binder chemical and blocked 1, 6 hexamethylene diisocyanate trimer is the coupling agent.

61. The combination of claim 57 further comprising one or more components selected from the group consisting of:

pigment, humectant, urea, urea and 2,3 propane diol, buffer, ammonium or sodium phosphates buffer, dispersant, defoamer, thickening agent, cross-linking agent, softening agent, carbon black, UV absorbing material, anti-scuffing agent, a silicone or fluoropolymer, light spill-suppressing agent, anti-static agent, water repellent agent, a silicone, and a fluoropolymer.

62. The combination of claim 57 wherein the volume ratio of the binder to the microbeads is equal to or less than 50%.

63. The combination of claim 57 wherein essentially all of the microbeads are unmetallised and the retroreflective elements include reflective flake particles.
64. The combination of claim 57 wherein the binder forms at least part of a liquid carrier medium for the retroreflective elements or microbeads.
65. The combination of claim 57 wherein the binder chemicals, retroreflective elements and microbeads are comprised of a one-pack retroreflective ink or a two-pack retroreflective ink having the coupling agent as the second pack.
66. The combination of claim 65 wherein the two-pack ink includes a reactive polyisocyanate or an alkoxysilyl alkyl derivative.
67. The combination of claim 57 wherein the microbeads are metallised with an aluminium coating that is superposed on stannous chloride.
68. The combination of claim 67 wherein the microbeads are treated with a compound selected from the group consisting of a silicate, a sodium silicate, a silane, an amino silane, a bis-[*gamma*-(trimethoxysilyl) propyl] amine and stannous chloride.
69. The combination of claim 67 wherein the metallised microbeads are coated with a silicate or silane that is superposed on the metallised microbeads.
70. A composition that is a one-pack or a two-pack retroreflective ink which is comprised of the combination claimed in claim 57.

71. The composition of claim 70 wherein the retroreflective ink is water-based.
72. The composition of claim 71 that is suitably formulated for screen printing.
73. The composition of claim 70 wherein the ink has a viscosity that is less than or equal to about 40 pascals at room temperature.
74. A composition that is microbeads for use in the production of a retroreflective ink, the microbeads having applied thereto one or more of the group comprising silicate, a silane, an amino silane, bis-[*gamma*-(trimethoxysilyl) propyl] amine and stannous chloride.
75. The composition of claim 74 wherein the microbeads are metallised with a coating of aluminium superposed on the stannous chloride.
76. The composition of claim 75 wherein the silicate is superposed on the metallised aluminium coated beads and the silane is superposed on the silicate.
78. The composition of claim 74 wherein the microbeads have one or more of the following characteristics selected from the group consisting of: a refractive index in the range of about 1.8 to 2.2, a median size of the microbeads in the range of about 10 to 100 microns and the microbeads are composed of titanium glass or barium glass.
79. A composition that is a retroreflective ink which contains microbeads as claimed in claim 74.
80. The composition of claim 78 which includes binder chemicals for attaching the

microbeads to a substrate to which the ink is to be applied.

81. ✓ The composition of claim 80 which includes a coupling agent for coupling the microbeads and for cross-linking the binder chemicals, the coupling agent being unreactive until the printing process is carried out.

82. ✓ A method for making a one-pack retroreflective ink comprising the steps of:

- (a) making microbeads;
- (b) suspending the microbeads in a liquid carrier medium, the liquid carrier medium is comprised of binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied and a coupling agent which couples the microbeads and cross-links the binder chemicals, the coupling agent being unreactive except at elevated temperature at which the printed substrate is cured.

83. ✓ The method of claim 82 wherein step (a) includes applying an aluminium coating to the microbeads.

84. ✓ The method of claim 83 wherein step (a) includes pre-treating the microbeads with stannous chloride prior to application of the aluminium coating.

85. ✓ The method of claim 84 wherein step (a) includes treating the microbeads with a dilute aqueous solution of stannous chloride.

86. ✓ The method of claim 82 wherein step (a) includes hemispherically metallising the microbeads in a vacuum metallising process in which the microbeads are held on a film with

an adhesive coating for transport through the metallising process, the adhesive coating is comprised of styrene-butadiene type adhesive.

87. The method according to claim 86 wherein step (a) includes passing the film through an aqueous solution of citric acid after metallisation..

88. The method of claim 86 wherein step (a) includes ultrasonically treating the film to assist in release of the microbeads from the adhesive .

89. The method of claim 85 wherein step (a) includes treating the microbeads prior to inclusion in the ink with a silicate.

90. The method of claim 82 wherein step (a) includes treating the microbeads with a silane or an amino silane prior to inclusion in the ink.

91. The method of claim 89 wherein step (a) includes treating the microbeads with a compound selected from the group consisting of a silane, an amino silane and bis-*[gamma*-(trimethoxysilyl) propyl] amine after the silicate treatment.

92. The method of claim 82 wherein step (a) includes adding an amino silanetriol or a blocked polyisocyanate to the liquid carrier medium as coupling agent.

93. The method of claim 82 wherein step (a) includes preparing the liquid carrier medium from the binder chemicals and the coupling agent before suspending the microbeads in the liquid carrier medium.



94. The method of claim 93 wherein the liquid carrier medium of step (b) includes additives selected from the group consisting of:

pigment, humectant, urea, urea and 2,3 propane diol, buffer, ammonium or sodium phosphate buffer, dispersant, defoamer, thickening agent, cross-linking agent, softening agent, carbon black, UV absorbing material, anti-scuffing agent, silicone, fluoropolymer, light spill-suppressing agent, anti-static agent and water repellent agent.

95. The method of claim 94 wherein step (b) includes adding a thickener to the liquid carrier medium before or after the addition of the binder chemicals and coupling agent.

96. A composition of an ink produced by the method of claim 82.

97. A composition of a substrate coated or printed with a composition of claim 96.

98. The composition of claim 97 wherein the substrate is a screen for displaying projected images or a studio background for chroma-keying applications.

99. The composition of claim 97 wherein the substrate is a flexible tape.

100. The method of providing a substrate having a retroreflective coating, comprising the steps of:

applying to the substrate an ink as claimed in claim 96 wherein the ink is formulated as a one-pack retroreflective ink and the coupling agent is activated after the ink is printed or coated on to the substrate.

101. The method of claim 100 wherein the coupling agent is activated by curing the ink coating at elevated temperature.

102. The method of claim 100 wherein the coupling agent is activated by UV light or other high energy radiation during or after the printing process.

103. A composition that is a retroreflective one-pack ink having a storage life of not less than about 3 months.

104. The composition of claim 103 wherein the retroreflective one-pack ink has a viscosity of between about 10 and 30 pascal after storage of not less than about 3 months.

105. The composition of claim 103 wherein the retroreflective one-pack ink has a laundering durability such that the retroreflectivity is not reduced by more than about 40% when applied to a substrate in the form of a cotton, nylon or polyester fabric and laundered for 5 cycles in accordance with ISO 6330, method 5A.

106. A composition of a fabric having fireproof or fire retardant properties that is printed or coated with a retroreflective ink which is comprised of retroreflective elements in a polymeric matrix, the fabric comprising a structural component that chars before it melts.

107. The composition of claim 106 wherein the fabric is made fireproof or fire retardant by application of a fire retardant agent.

108. The composition of claim 107 wherein the fire retardant agent is applied to a cellulosic, the fire retardant agent is selected from the group consisting of Proban ® and

Pyrovatex ®.

109. The composition of claim 106 wherein the fabric is comprised of an aramid fiber.

110. The composition of claim 106 wherein the fabric is non-burning after a retroreflective ink has been applied to the fabric.

111. The composition of claim 110 wherein the ink is aqueous-based and the polymeric matrix comprises polyvinylidene chloride.

112. The composition of claim 110 wherein the polymeric matrix comprises polyvinyl chloride or other non-flammable plastisol.

113. A composition that is a fireproof or fire retardant fabric printed or coated with a retroreflective ink which is comprised of retroreflective elements in a polymeric matrix, the fabric is comprised of a structural component that chars before it melts, the ink is comprised of an ink as claimed in claim 70.

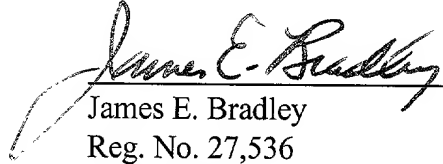
### **REMARKS**

Applicant submits, therefore, that claims 57-113 are in condition for allowance. Applicant respectfully request a speedy notice of allowance. If there are any outstanding issues, Applicant would appreciate a telephone call from Examiner.

Applicant believes that this Preliminary Amendment is being filed with a Section 371 application, therefore, a Petition for Extension of Time is not necessary. Notwithstanding, to the extent an additional extension of time is necessary, please consider this a petition therefor. Please charge any additional fees to deposit account no. 50-0259 (069918.000002),

Bracewell & Patterson, L.L.P.

Respectfully submitted,



James E. Bradley

Reg. No. 27,536

BRACEWELL & PATTERSON, L.L.P.

P.O. Box 61389

Houston, Texas 77208-1389

(713) 223-2900

Attorney for Applicants

Dated:

July 13, 2001

Applicant or Patentee: Brian Sagar  
Serial or Patent No.: Unknown Atty. Dkt. No.: 069918.000002  
Filed or Issued: Herewith  
For: Retroreflective Inks

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY  
STATUS (37 CFR 1.9(f) and 1.27(b)) - INDEPENDENT INVENTOR**

As a below named inventor, I hereby declare that I qualify as an independent inventor as defined in 37 CFR 1.9(c) for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, to the Patent and Trademark Office with regard to the invention entitled Retroreflective Inks described in

- ☐ the specification filed herewith  
☒ application serial no. PCT/GB00/00062, filed January 12, 2000  
☐ patent no. \_\_\_\_\_, issued \_\_\_\_\_

I have not assigned, granted, conveyed or licensed and am under no obligation under contract or law to assign, grant, convey or license, any rights in the invention to any person who could not be classified as an independent inventor under 37 CFR 1.9(c) if that person had made the invention, or to any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

- ☐ no such person, concern, or organization  
☐ persons, concerns or organizations listed below\*

\*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

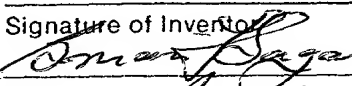
FULL NAME Reflec plc  
ADDRESS Road One, Winsford Industrial Estate, Winsford, Cheshire CW7 3QQ, GB  
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

FULL NAME \_\_\_\_\_  
ADDRESS \_\_\_\_\_  
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

FULL NAME \_\_\_\_\_  
ADDRESS \_\_\_\_\_  
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed

Brian Sagar		
NAME OF INVENTOR	NAME OF INVENTOR	NAME OF INVENTOR
Signature of Inventor 	Signature of Inventor	Signature of Inventor
Date <u>27 June '07</u>	Date	Date

Applicant or Patentee: Brian Sagar

Small Business Concern:

Serial or Patent No.: Unknown

Filed or Issued: Herewith

For: Retroreflective Inks

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY  
STATUS (37 CFR 1.9(f) and 1.27(b)) SMALL BUSINESS CONCERN**

I hereby declare that the herein-identified small business concern qualifies as a small business concern as defined in 13 C.F.R. 121.3-18, and reproduced in 37 C.F.R. 1.9 (d), for purposes of paying reduced fees under section 41 (a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled **RETROREFLECTIVE INKS** by inventor(s) **Brian Sagar** described in:

- ☐ the specification filed herewith.
- ☐ the application identified above.
- ☐ the patent identified above.

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below and no rights to the invention are held by any person, other than the inventor(s), who could not qualify as a small business concern under 37 C.F.R. 1.9 (d) or a nonprofit organization under 37 C.F.R. 1.9 (e).

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 C.F.R. 1.28 (b))


I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME AND TITLE OF PERSON SIGNING:

FULL NAME: PETER ALAN WHITE

TITLE: MANAGING DIRECTOR

ADDRESS: REVELLEY ROAD ONE WINSFORD IND SST WINSFORD CHESHIRE

SIGNATURE:  DATE: 18/06/01

☒ Individual ☐ Small Business Concern ☐ Nonprofit Organization

## RETROREFLECTIVE INKS

This invention relates to retroreflective inks and methods for making them.

Retroreflective coating compositions have been the subject of numerous patents, for example US Patents 2 963 378, Palmquist *et al*, 3 099 637, 3 228 897 and 3 420 597, Nellessen, 3 535 019, Longlet *et al* and 4 103 060 and 4 263 345, Bingham *et al*. A retroreflective ink has been commercially available for a number of years, marketed by the 3M company, this product being available in dark grey and sold as a three pack system, comprising a binder dispersion system, a pack of hemispherically coated glass microspheres or beads and a coupling agent, which are mixed just prior to use.

One pack inks were proposed in WO 94/06869, M N Ellis and in EP 0 729 592, Reflective Technology Industries Limited and US 5 650 213, Reflective Technology Inc., which also disclose the incorporation of pigment. US 5 650 213 specified a range of pigment particle size which is what is, in fact, the usual range commercially available, and ranges of binder/bead and binder/(bead and pigment) volume ratios which are seemingly the ranges of choice to produce an ink which is printable by conventional screen printing techniques.

Problems associated with the performance of reflective coatings, especially in the convenient, one-pack form that does not require mixing just prior to printing, involve shelf life, washfastness and abrasion resistance. These key areas are interrelated - the binder system must be such as will not allow the beads to settle even over extended storage periods, and it must also not couple to the beads during that storage, yet it must, on printing, adhere the beads to the substrate in a reasonably washfast and abrasion



resistant manner while permitting the beads to be exposed appropriately to retroreflect light.

The severity of these problems may explain the sale by 3M of the three pack system and the fact that the inks produced according to US 5 650 213 are formulated solely for the production of printed fabric by the patentee Reflective Technology Inc. and not for sale to printers.

The present invention addresses these - and other - problems and provides long shelf life one pack retroreflective ink systems with good washfastness and abrasion resistance.

According to one aspect of the present invention there is provided the combination of ingredients, especially for use in the formulation of a one or two-pack retroreflective ink, comprising retroreflective elements, microbeads additional to said retroreflective elements and/or constituting said retroreflective elements at least in part, binder chemicals for attaching the retroreflective elements and microbeads to a substrate to which the ink is to be applied, and a coupling agent for coupling the microbeads and cross-linking the binder chemicals, the coupling agent being unreactive until the printing process is carried out.

A one-pack ink produced using the above combination of ingredients may have a storage life of not less than 3 months, preferably not less than 6 months and more preferably not less than 12 months when stored under ambient conditions (i.e. a temperature of about 20°C). Also such inks, when stored for prolonged periods of 3 months or more under ambient conditions, show no significant change in rheology while retaining adequate retroreflectivity properties and durability to laundering. Thus, a retroreflective one-pack ink in accordance with the invention may retain a viscosity of between 10 and 30 pascal after storage for not less than 3 months, preferably not less

than 6 months and more preferably not less than 12 months, and may also exhibit laundering durability such that retroreflectivity is not reduced by more than 40% (preferably by not more than 30% and more preferably by not more than 20%) when applied to a substrate in the form of a cotton, nylon or polyester and laundered for 5 cycles in accordance with ISO 6330, method 5A.

The coupling agent is usually one which is substantially unreactive at ambient temperature, namely 20°C. Typically the coupling agent is unreactive except at elevated temperature at which the printed substrate is cured, e.g. a temperature within the range of 60 to 200°C, e.g. 130 to 180°C.

The coupling agent may be rendered active by elevated temperature; however, we do not exclude the possibility that the coupling agent may be rendered active by other means such as exposure to UV light or other high energy radiation.

Typically the binder is polymeric and the coupling agent serves to couple the beads to the polymeric binder.

Viewed from another aspect, the invention resides in a one-pack or a two-pack retroreflective ink comprising microbeads in a liquid carrier medium including binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied, the microbeads being incorporated in the carrier medium, and a coupling agent which couples the microbeads and cross-links the binder chemicals, characterised in that the coupling agent is not activated until the ink is printed.

The two-pack system comprises a separate pack for the coupling agent.

The ink may comprise retroreflective and/or non-retroreflective microbeads. Typically the proportion of microbeads which do not have a retroreflective coating constitute no more than 50% by volume of the total microbead content but may be up to 100% when reflective flakes are used in conjunction with microbeads to provide retroreflectivity.

The binder and coupling agent may be selected from, but is not limited to, the following combinations:

polyvinylidene chloride copolymer as binder and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent;

an acrylic copolymer as binder and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent; and

polyurethane as binder and blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent.

The microbeads may have an aluminium coating, and may be pre-treated with a silicate before inclusion in the ink. They may for instance be pretreated with sodium silicate. They may be treated with a silane, especially a silane having a reactive group such as an amino group, which treatment may be after a silicate treatment and before inclusion in the ink. A suitable amino silane is bis-*[gamma*-(trimethoxysilyl) propyl] amine.

The ink may comprise pigment, and may, especially when comprising pigment, comprise non-retroreflective, which usually means un-metallised, microbeads. The pigment content is typically up to 5% by weight of the ink.

The microbeads may be pretreated before metallisation with stannous chloride.

The ink may be formulated - as to, e.g. viscosity, particle size - suitably for screen printing. The microbeads may have a median size in the range of 10 to 100 microns, e.g. 25 to 70 microns. Typically in the case of inks using metallised retroreflective microbeads, the median size is about 40 microns whereas in the case of inks using non-retroreflective microbeads in conjunction with other reflective elements such as reflective flake particles, the microbeads typically have a median size of about 60 microns.

The microbeads, whether retroreflective or not, are preferably composed of high refractive index glass, such as a titanium/barium based glass with a refractive index in the range of 1.8 to 2.2, e.g. about 1.9.

The ink may comprise a humectant, which may comprise urea and/or 2,3 propane diol, and may be water-based. It may comprise a buffer, to ensure an appropriate pH, such buffer, for example, comprising an ammonium phosphate buffer or a sodium phosphate buffer. A dispersant may also be included, as may a defoamer, a thickening agent, a cross-linking agent and a softening agent.

Other constituents that may be present in the ink may be selected from the group comprising carbon black; UV absorbing material; anti-scuffing agent, optionally a silicone or fluoropolymer; light spill-suppressing agent; anti-static agent and water repellent agent, optionally a silicone or fluoropolymer.

Non-water based inks may also be comprised within the invention. In this case, the need to protect the aluminium coating against attack in water-based media may be less important.

Surprisingly, having regard to the teaching of US 5 650 213, substantially better quality inks - in terms of reflectivity, washfastness, abrasion resistance and shelf life - are produced with binder to bead volume ratios equal to or less than 50%. Essentially, more beads can be attached using less obscuring binder, more firmly and more permanently than when the prior art binder to bead ratios are used.

For a screen printing ink, the viscosity is desirably equal to or less than 40 pascals, preferably between 10 and 30 pascals, at room temperature.

The invention also comprises a method for making a one-pack retroreflective ink comprising the steps of:

- making microbeads;
- suspending the microbeads in a liquid carrier medium;
- the liquid carrier medium comprising binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied and a coupling agent which couples the microbeads and cross-links the binder chemicals, the coupling agent being unreactive except at elevated temperature (e.g. within the range from 60 to 200°C and usually from 130 to 180°C) at which the printed substrate is cured.

The method may involve the application of an aluminium coating to glass microbeads. The microbeads may be pretreated with stannous chloride prior to application of the aluminium coating, and may be treated with a dilute solution of stannous chloride.

The microbeads may be hemispherically metallised in a vacuum metallising process in which they are held on a film with an adhesive coating for transport through the metallising process, the adhesive coating comprising a styrene/butadiene type or other adhesive, which loses its tack when wet. The film may comprise a polyester or polyolefin film. Following metallisation, the film may be passed through an aqueous solution of citric acid or other aqueous solution with a  $pK_a$  value of around 2, and may be treated ultrasonically to assist in release of the microbeads from the adhesive surface. In contradistinction to other methods for attachment of beads for metallisation, this method is easier at least inasmuch as the citric acid bath can be re-used over and over without replenishment.

The microbeads may be treated prior to inclusion in the ink with a silicate, which may be a dilute aqueous solution of sodium silicate. The beads may also (with or without such sodium silicate treatment) be treated with a silane such as an amino silane prior to inclusion in the ink, and such silane treatment may follow the silicate treatment. A particularly beneficial amino silane is bis-[*gamma*-(trimethoxysilyl) propyl] amine. These treatments, severally and collectively, appear to enhance the permanence of the attachment of the aluminium coating to the microbeads and of the microbeads to the substrate on printing.

An aminoalkyl silanetriol and/or a blocked polyisocyanate may be added to the liquid carrier medium as coupling agent.

In the event, see below, that a two-pack, rather than a one-pack system is required, an alkoxysilyl alkyl derivative such as an amino silane - which could be the same amino silane used to treat the microbeads - and/or a polyisocyanate (typically where the microbeads are amine treated) may also be added to the liquid carrier medium as coupling agent,

In the preparation of the ink, a liquid carrier medium may be prepared comprising binder chemicals and coupling agent, the microbeads being added to the medium. A pigment may be added to the medium containing the microbeads.

Further additive or additives to be incorporated in the liquid carrier medium, may be selected from the group comprising:

pigment; humectant, optionally urea and/or 2,3 propane diol; buffer, optionally based on ammonium or sodium phosphates; dispersant; defoamer; thickening agent; cross-linking agent; softening agent; carbon black; UV absorbing material; anti-scuffing agent, optionally a silicone or fluoropolymer; light spill-suppressing agent; anti-static agent and water repellant agent, optionally a silicone or fluoropolymer.

Where a thickener is included, it may be added to the medium in two steps, namely before and after the addition of the binder and coupler.

According to a further aspect of the invention there is provided microbeads for use in the production of a retroreflective ink, the microbeads having silicate (optionally sodium silicate) and/or silane (optionally an amino silane such as bis-[*gamma*-(trimethoxysilyl) propyl] amino) and/or stannous chloride applied thereto.

The microbeads may be metallised, optionally with a coating of aluminium, the metal being superposed on the stannous chloride.

The microbeads may be metallised, optionally with a coating of aluminium, the silicate and/or silane being superposed on the metallised beads and the silane where present being superposed on the silicate where present.

Also within the scope of the invention is an ink incorporating such microbeads and substrates such as fabrics coated or printed with inks in accordance with the various aspects of the invention.

For certain applications, notably where printed or coated with retroreflective inks, for example for backdrops and special effects screens in film and television studios, it is desirable that fabrics used are fireproof, or fire retardant.

The specialised nature of some retroreflective inks, however, raises problems in connection with many normally fireproof or fire retardant fabric materials.

Another aspect of the invention is concerned with a fireproof or fire retardant fabric printed or coated with retroreflective ink that is particularly satisfactory as a backdrop or screen in the applications in question.

The invention comprises a fireproof or fire retardant fabric printed or coated with a retroreflective ink which comprises retroreflective elements in a polymeric matrix, the fabric comprising a structural component that chars before it melts.

The fabric may be made fireproof or fire retardant by application of a fire retardant agent, such as the commercially available Proban ® or Pyrovatex ®, to cellulose, or it may be naturally fireproof or fire retardant, such as an aramid.

The ink is desirably non-burning, at least once applied to the fabric. The polymeric matrix may comprise polyvinylidene chloride (e.g. in the case of an aqueous-based ink), or polyvinyl chloride or other non-flammable plastisol.



Examples of suitable inks for this purpose are given hereinafter in Tables 2 and 3.

Substrates coated with inks in accordance with various aspects of the present invention may find use in a variety of applications such as flexible tape having a retroreflective coating, for instance tape as used in defining boundary lines and/or cordoning off areas such as crime scenes, construction sites, road works and other hazards.

Another important application is retroreflective materials materials for use as studio background material for chroma-keying and like purposes, as disclosed in GB-A-2312565 and GB-A-2321814 the disclosures of which are incorporated herein by this reference. Thus, a substrate in the form of a flexible sheet material may be coated or printed with an ink in accordance with the present invention to produce a studio background material exhibiting a normalised retro-reflectivity of at least about 1/4 at an angle of incidence of at least 60 degrees to the normal, i.e. as described in GB-A-2312565 and GB-A-2321814.

A substrate provided with a retroreflective coating in accordance with the present invention may be provided with an additional coating or coatings for protecting the retroreflective coating against scuffing and/or moisture (i.e. a water repellant coating), e.g. a fluoropolymer coating applied over the retroreflective coating. An anti-static coating may also be applied to the substrate. Alternatively, instead of coating the substrate with such coatings after printing or coating the substrate with retroflecive ink, the ink may incorporate ingredients which will confer anti-scuffing, water repellant and/or anti-static properties.

The substrate may be selected from a wide range of materials including textile fabrics (e.g. woven or knitted) such as cotton, polyesters, nylons, silk, wool, viscose and acrylics.

Inks and methods for making them, according to the invention, will now be described with reference to the accompanying drawings, in which Figure 1 is a diagrammatic illustration of the production of metallised beads; and Figure 2 is a block diagram of a process for making an ink.

Examples of ink formulations according to the invention are given in Tables 1 to 4.

**Table 1** - Inks based on a acrylic copolymer binder system and (3-aminopropyl) silanetriol coupling agent

<b>Ingredient/Ink reference</b>	<b>C202</b>	<b>C205</b>	<b>C208</b>
Urea (Humectant)	10	10	10
Water	154	179	179
Ammonium phosphate buffer	20	20	20
Alcoprint PDN (Dispersant)	2	2	2
Agitan 218 (Defoamer)	2	2	2
Alcoprint PT21 (Thickening agent)	8	8	8
2,3 Propane diol (Humectant)	25	25	25
Alcoprint PFL (Trimethoxymethyl melamine cross-linking agent)	15	15	15
Alcoprint PSM (Softening agent)	30	30	30
Alcoprint PBA (Acrylic copolymer binder)	300	225	225
Ammonium hydroxide	1	1	1
Silquest VS-142 (3-aminopropyl silanetriol coupling agent)			
[20% in water]	25	25	25
Alcoprint PT21 (Thickening agent)	6	3	4.6
Metallised beads (40 micron) treated with sodium silicate and Silquest A-1170 (Bis[trimethoxysilylpropyl])			

- 12 -

amine)	400	450	400
Nonmetallised beads (40 micron) treated with sodium silicate and Silquest A-1170	--	--	50
<b>Total</b>	997	995	996.6
Binder volume %	12	9	9
Bead volume %	16	18	18
Binder volume/bead volume %	75	50	50
Viscosity	20.7	16.2	23.2
Temperature	16.6	16.6	16.6
pH	8.4	8.9	8.8

**Table 2 -** Inks based on a polyvinylidene chloride copolymer binder system and (3-aminopropyl) silanetriol coupling agent

<b>Ingredient/Ink reference</b>	<b>V246</b>	<b>V248</b>	<b>V251</b>
Urea (Humectant)	10	10	10
Water	128	288	288
Ammonium phosphate buffer	20	20	20
Emulsifier WN (Dispersant)	3	3	3
Agitan 218 (Defoamer)	2	2	2
Alcoprint PT21 (Thickening agent)	8	8	8
2,3 Propane diol (Humectant)	25	25	25
Polidene 33-048 (Binder)	273	163	163
Ammonium hydroxide	1.4	1.4	1.4
Silquest VS-142 (Coupling agent)			
[20% in water]	25	25	25
Alcoprint PT21 (Thickening agent)	3	5	3
Metallised beads (40 micron) treated with sodium silicate and Silquest A-1170	500	450	400
Non-metallised beads (40 micron) treated with sodium silicate and Silquest A-1170	--	--	50
<b>Total Weight of Ink (g)</b>	<b>998.4</b>	<b>1,000.4</b>	<b>998.4</b>
Binder volume %	15	9	9
Bead volume %	20	18	18
Binder volume/bead volume %	75	50	50
Viscosity (pascals)	25.6	14.2	12.3
Temperature (°C)	17.7	17.6	17.2
pH	8.6	8.7	8.7

**Table 3 -** Inks based on a polyvinylidene copolymer binder system and a combination of (3-aminopropyl) silanetriol and blocked hexamethylene diisocyanate trimer coupling agents

<b>Ingredient/Ink reference</b>	<b>V253</b>	<b>V254</b>	<b>V257</b>
Urea (Humectant)	10	10	10
Water	91	183	183
Ammonium phosphate buffer	20	20	20
Emulsifier WN (Dispersant)	2	2	2
Emulsifier HVN (Dispersant)	2	2	2
Agitan 218 (Defoamer)	2	2	2
Alcoprint PT21 (Thickening agent)	9.3	8	8
2,3 Propane diol (Humectant)	25	25	25
Polidene 33-048 (Binder)	273	181	181
Ammonium hydroxide	1.4	1.4	1.4
Silquest VS-142 (Coupling agent)			
[20% in water]	25	25	25
Trixene BI 7986 (Coupling agent)	40	40	40
Alcoprint PT21 (Thickening agent)	--	--	--
Metallised beads (40 micron) treated with sodium silicate and Silquest A-1170	500	500	400
Non-metallised beads treated with sodium silicate and Silquest A-1170	--	--	100
<b>Total Weight of Ink (g)</b>	<b>1,000.7</b>	<b>999.4</b>	<b>999.4</b>
Binder Volume %	15	10	10
Bead Columes %	20	20	20
Binder Volume/Bead Volume Ratio %	75	50	50
Viscosity (pascals)	22.5	22.1	21.2
Temperature (°C)	19.3	19.0	19.0
pH	8.4	8.3	8.4

**Table 4** - Inks based on a polyurethane binder system and a blocked 1,6 Hexamethylene diisocyanate trimer coupling agent

<b>Ingredient/Ink reference</b>	<b>P96</b>	<b>P98</b>	<b>P102</b>
Urea (Humectant)	10	10	10
Water	62	187	187
Sodium Phosphate Buffer	10	10	10
Emulsifier WN (Dispersant)	3	3	3
Agitan 218 (Defoamer)	2	2	2
Alcoprint PT21 (Thickener)	3.0	3.1	3.0
2,3 Propane diol (Humectant)	25	25	25.1
Alcoprint PSM (Softener)	30	30	30
Witcobond 769 (Binder)	300	225	226
Trixene BI-7986 (Coupler)	50	50	50
Alcoprint PT21 (Thickener)	0.7	4.0	3.0
Metallised beads treated with sod.silicate and Silquest A-1170	500	450	400
Non-metallised beads treated with sod.silicate and Silquest A-1170	--	--	70
<b>Total Weight of Ink (g)</b>	<b>993.7</b>	<b>999.1</b>	<b>1,019.1</b>
Binder Volume %	12	9	8.8
Bead Volume %	60	18	18.5
Binder Volume/Bead Volume Ratio %	60	50	47.9
Viscosity (pascals)	O/R	31.0	32.0
Temperature (°C)	18.8	18.2	18.5

Generally speaking, the ingredients are added in the tabulated order given in Tables 1 to 4. The thickener is added in two stages. Pigment, not tabulated, is added at the end in suitable quantity to yield the desired colour.

Viscosities were measured with a Brookfield viscometer using a number 5 spindle rotating at 10 rpm.

Table 5 lists the chemical nature and sources of proprietary products used in the inks of Tables 1 to 4.

**Table 5**

<b>Ink Component</b>	<b>Proprietary Product</b>	<b>Chemical Nature</b>	<b>Supplier</b>
Binder	Alcoprint PBA	Aqueous emulsion of an acrylic copolymer	Allied Colloids
	Polidene 33-048	Aqueous emulsion of a vinylidene chloride/acrylate copolymer	Scott Bader
	Witcobond 769	Water based polyurethane dispersion	Baxenden
Cross-linking/ coupling agent	Alcoprint PFL	Trimethoxymethyl melamine	Allied Colloids
	Silquest VS-142	3-Aminopropyl silanetriol	OSi Specialities/ Ambersil Ltd.
	Silquest A-1170	bis-trimethoxysilylpropyl) amine	OSi Specialities/ Ambersil Ltd.
	Trixene BI-7986	Blocked 1,6 hexamethylene diisocyanate trimer	Baxenden
Softening agent	Alcoprint PSM		Allied Colloids
Thickening agent	Alcoprint PT21	Dispersion of an acrylic copolymer in light mineral oil	Allied Colloids
Dispersant	Alcoprint PDN	Aqueous solution of an anionic acrylic polymer	Allied Colloids
	Emulsifier WN	Nonionic arylpolyglycol ether	Bayer

Ink Component	Proprietary Product	Chemical Nature	Supplier
	Emulsifier HVN		BASF
Defoaming agent	Agitan 218		Munzing Chemie

Retroreflective microbeads are made, according to one aspect of the invention, by a process which is generally similar to the one that has been used commercially for many years, namely by embedding glass microspheres in an adhesive layer on a substrate and coating the exposed surface of the microspheres with an aluminium layer in a vacuum metalliser. There are, however, subtle, but important differences. The method according to the invention, which is novel and inventive *per se* for the manufacture of hemispherically coated microbeads, regardless of any ink formulation in which they will be used is illustrated by way of example in Figure 1.

A carrier material 11, which is for example a polyester film, supplied on a reel 11a, which may contain, say, 1000m of film of width 1500mm, is coated by contact with a lick roller 12 dipping into a bath 13 with an 18 micron layer 14 of a styrene/butadiene type adhesive 15, the coating thickness being determined e.g. by a doctor blade/roller arrangement 16.

Beads 17 (see inset to Figure 1) are scattered on the adhesive layer 14 from a hopper 18 and pressed into the adhesive layer 14 by a roller arrangement 19. Excess beads are removed e.g. by suction arrangement 20.

Glass beads of refractive index 1.9, size 40 microns are used, and, after the roller arrangement 19, appear, in cross-section, as shown in the inset.



The beaded carrier material 11 is then passed through a vacuum metalliser 21 to be coated with aluminium to a thickness of about 0.3 microns. The material 11, wound on a reel, is placed in the vacuum metalliser and run off on to a take-up reel to which it is secured; then the metalliser is evacuated and the aluminium source energised and the material passed reel-to-reel to expose it to the aluminium vapour. The coated, beaded carrier 11 is then passed through a bath 22 of aqueous solution (1%) of citric acid at a temperature of 40 - 50°C, passing over a series of rollers 23 to provide a dwell time in the bath of several minutes. The material 11 also passes over an ultrasonic plate 24 which aids release of the microbeads which fall to the bottom of the bath 22. At the end of the run of 1000m of carrier 11, the microbeads are sucked out of the bottom of the bath 22, rinsed with water and dried.

The effect of the citric acid bath is to cause the styrene/butadiene adhesive to lose its tack and release the microbeads. The material 11 regains its tack on drying, and can be re-used for further runs of bead manufacture without the need for further coating. The citric acid bath 22 can likewise be reused without replenishment of the citric acid.

Prior to coating, the glass beads are pre-treated with a dilute aqueous solution of stannous chloride, followed by drying and resieving. It is found that this gives significant improvement in the durability of the reflectivity of a printed design.

After coating, the beads are treated with a dilute aqueous solution of sodium silicate. It is thought that the treatment passivates the aluminium coating, reducing its susceptibility to attack in aqueous environments, while, at the same time, the sodium silicate reacts with the titanium/barium glass and/or the aluminium increasing the number of reactive sites on the surface of the coated microbeads that are available for reaction with the coupling agent in the ink.

If this sodium silicate treatment is carried out close to the metallisation process, the beads from that process can be used after rinsing but before drying. About 40 kg wet metallised beads (containing some 10 kg water) are mixed with a solution of 20 kg water containing 1.4 kg sodium silicate and stirred for 5 minutes. The beads are then allowed to settle, the sodium silicate solution decanted off, the beads rinsed with tap water, with a final rinse in deionised water.

Significant improvement in washfastness, especially with low (e.g. below 0.5%) levels of certain coupling agents in the formulation (which considerably improves shelf life), is obtained by further treatment of the metallised beads with amino silanes, significantly bis-*[gamma*-(trimethoxysilyl) propyl] amine.

The combined effect of these bead preparation treatments is to provide an ink with a shelf life well in excess of 12 months yet which exhibits insignificant loss of retroreflectivity after multiple washings at 40°C, even if the amount of coupling agent is as low as 0.5%.

Figure 2 is a block diagram of production steps for a typical ink according to the invention, the steps being :

- 30 Glass microbead production, with any necessary sieving to a desired size range - about 40 microns is an ideal size;
- 31 Stannous chloride pre-treatment, drying;
- 32 Metallising;
- 33 Recovery in citric acid solution;
- 34 Rinsing;
- 35 Drying;
- 36 Sodium silicate treatment of metallised beads;

- 37 Rinsing;
- 38 Amino silane pre-treatment;
- 39 Mixing liquid carrier medium;
- 40 Add treated metallised (and, if desired, umetallised) beads to carrier medium;
- 41 Add pigment;

Ink formulations detailed herein, formulated by the methods described, operating as one-pack systems, have long shelf lives, being usable after more than six months, in many cases after more than a year after formulation (based on accelerated ageing measurements at elevated storage temperatures). They show higher initial retroreflectivities at the lower binder/bead volume ratios made possible by the various measures described.

Washfastness and abrasion resistance are acceptable with binder volumes as low as 9% - reducing binder content in the formulation containing polyvinylidene chloride and Trixene actually increases abrasion resistance.

The various novel ingredients and combinations of ingredients each have their contributions to make in connection with the production of one pack inks and while the importance of a binder combined with a coupling agent reacting only at elevated temperature has been particularly noted, it is not intended to suggest that that might be the only novel and inventive subject matter disclosed herein. The pre-treatment of the beads both before and after metallisation also has profound effects even with the binder/coupler systems and is of advantage also in the preparation of inks for printing on substrates which will not withstand elevated temperatures. Here it is necessary to resort to a two-pack system, with the coupling agent mixed into the ink just before printing. A reactive polyisocyanate may be used as a coupling agent in such circumstances. A

two-pack arrangement is, of course, more convenient to use than the old three-pack system, and is made possible by bead pre-treatment.

Where unmetallised beads are added - giving the effect, quite obviously, of reducing overall retroreflectivity, but reducing the greyness associated with metallised beads and therefore enhancing the colour brightness of pigmented inks, the unmetallised beads also benefit from the bead pre-treatment, particularly treatment with silicate and silane. .

Unmetallised beads may also be used in similar formulation, and having had similar pre-treatment, without metallised beads but with flake particles having a mirror-like finish. Such a coating composition, said to be suitable for application by brushing, was described in US 3 835 087, Searight *et al*, issued 10 September 1974, and printing ink of this description is commercially available.

According to the present invention, in another aspect, one-pack inks containing unmetallised glass microspheres and flake particles comprise a liquid carrier medium including binder chemicals for attaching the microbeads and flake particles to a substrate to which the ink is to be applied and a coupling agent which couples the microbeads and cross-links the binder chemicals, characterised in that the coupling agent is unreactive except at elevated temperature at which the ink of the substrate is cured.

Binder and coupler systems as described above are suitable, and the microbeads benefit in the same way from the sodium silicate and amino silane pre-treatment - the stannous chloride pre-treatment is unnecessary.

A preferred flake material is Iriodin 123 - mica flake coated with titanium dioxide, supplied by Merck. The optimum particle size is 5-35 microns, and the flake may be present in an amount about 7.5% by weight.

Mean glass microbead size may be 60 micron - larger beads, e.g. up to 70 micron and larger may be used but may not be suitable for finer screen printing mesh sizes. Good quality, e.g. 1.9 refractive index, beads give better results than lower refractive index beads, and best results are obtained using 60 micron TSTF (twice sieved twice fired) beads.

Coloured reflectivity can be achieved by using interference pigments (Iriodin 200 series), while gold lustre mica pigments (Iriodin 300 series) and metal lustre pigments (Iriodin 500 series) give interesting effects particularly when printed on coloured fabrics.

Table 6 lists ingredients for a range of such inks.

**Table 6**

<b>Ingredient/Ink reference</b>	<b>NMB155</b>	<b>NMB182</b>	<b>NM B185</b>	<b>NMB191</b>
Urea (Humecant)	10	10	10	10
Water	79	134	94	91
Ammonium phosphate buffer	20	20	20	--
Sodium phosphate buffer	--	--	--	10
Emulsifier WN (Dispersant)	--	3	2	3
Emulsifier HVN (Dispersant)	--	--	2	--
Alcoprint PDN (Dispersant)	2	--	--	--
Agitan 218 (Defoamer)	2	2	2	2
Alcoprint PSM (Softener)	30	--	--	30
Alcopriny PT21 (Thickener)	4	4.8	3.3	3
2,3 Propane diol (Humectant)	25	25	25	25
Alcoprint PFL (Cross-linker)	15	--	--	--
Alcoprint PBA (Binder)				
[acrylic]	300	--	--	--
Polidene 33-048 (Binder)				
[polyvinylidene chloride]	--	300	300	--
Witcobond 769 (Binder)				
[polyurethane]	--	--	--	300
Trixene BI-7986 (Coupling agent)	--	--	40	50
Ammonium hydroxide	1	1.4	1.4	--
Silquest VS-142 (Coupling agent) [20% in water]	25	25	25	--
Alcoprint PT21 (Thickener)	3.5	--	--	1
Iriodin 123 [Mica coated with titanium dioxide]	75	75	75	75
Beads (60 micron) treated with sod.sil.+ A-1170	400	400	400	400
<b>Total weight (g)</b>	<b>991.5</b>	<b>1000.2</b>	<b>999.7</b>	<b>1000.0</b>
Viscosity (pascals)	23.6			
pH	8.5			

### CLAIMS

1. The combination of ingredients, especially for use in the formulation of a one or two-pack retroreflective ink, comprising retroreflective elements, microbeads additional to said retroreflective elements and/or constituting said retroreflective elements at least in part, binder chemicals for attaching the retroreflective elements and microbeads to a substrate to which the ink is to be applied, and a coupling agent for coupling the microbeads and cross-linking the binder chemicals, the coupling agent being unreactive until the printing process is carried out.
2. The combination of Claim 1 in which the coupling agent is unreactive except at elevated temperature at which the printed substrate is cured.
3. The combination of Claim 1 or 2, at least some of the microbeads being without a retroreflective coating.
4. The combination of Claim 1, 2 or 3 in which the binder/coupling agent system is selected from the group comprising:
  - polyvinylidene chloride copolymer as binder and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent;
  - an acrylic copolymer as binder and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent; and
  - polyurethane as binder and blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent.
5. The combination of any one of Claims 1 to 3 further comprising one or more components selected from the group comprising:

pigment; humectant, optionally urea and/or 2,3 propane diol; buffer, optionally based on ammonium or sodium phosphates; dispersant; defoamer; thickening agent; cross-linking agent; softening agent; carbon black; UV absorbing material; anti-scuffing agent, optionally a silicone or fluoropolymer; light spill-suppressing agent; anti-static agent and water repellant agent, optionally a silicone or fluoropolymer.

6. The combination of any one of Claims 1 to 5 in which the binder volume to bead volume ratio is equal to or less than 50%.
7. The combination of any one of Claims 1 to 6 in which the microbeads are all or essentially all unmetallised and the retroreflective elements comprise reflective flake particles.
8. The combination of any one of Claims 1 to 7 in which the binder forms at least part of a liquid carrier medium in which the retroreflective elements and/or microbeads are incorporated.
9. The combination as claimed in any one of Claims 1 to 7 in which the binder chemicals and retroreflective elements/microbeads comprise one pack retroreflective ink or a two-pack retroreflective ink with the coupling agent comprising the second pack.
10. The combination of Claim 9, being a two pack ink in which the coupling agent comprises a reactive polyisocyanate and/or an alkoxysilyl alkyl derivative.
11. The combination of any one of Claims 1 to 10, the microbeads having silicate (optionally sodium silicate) and/or silane (optionally an amino silane such as bis-[*gamma*-(trimethoxysilyl) propyl] amino) and/or stannous chloride applied thereto.



12. The combination of Claim 11 in which the microbeads are metallised, optionally with a coating of aluminium, the metal being superposed on the stannous chloride.

13. The combination of Claim 11 or 12 in which the microbeads are metallised, optionally with a coating of aluminium, the silicate and/or silane being superposed on the metallised beads and the silane where present being superposed on the silicate where present.

14. A one or two-pack retroreflective ink comprising the combination claimed in any one of Claims 1 to 13.

15. An ink as claimed in Claim 14, being water-based.

16. An ink as claimed in Claim 14 or 15, formulated suitably for screen printing.

17. An ink as claimed in Claim 14, 15 or 16 of which the viscosity is less than or equal to 40 pascals, preferably between 10 and 30 pascals, at room temperature.

18. Microbeads for use in the production of a retroreflective ink, the microbeads having silicate (optionally sodium silicate) and/or silane (optionally an amino silane such as bis-[*gamma*-(trimethoxysilyl) propyl] amino) and/or stannous chloride applied thereto.

19. Microbeads as claimed in Claim 18 which are metallised, optionally with a coating of aluminium, the metal being superposed on the stannous chloride.

20. Microbeads as claimed in Claim 18 or 19 which are metallised, optionally with a coating of aluminium, the silicate and/or silane being superposed on the metallised beads and the silane where present being superposed on the silicate where present.

21. Microbeads as claimed in any one of Claims 18 to 20 having one or more of the following characteristics: a refractive index in the range of 1.8 to 2.2, preferably about 1.9; in the form of beads having a median size in the range of 10 to 100 microns, preferably 25 to 70 microns; and composed of titanium/barium glass.

22. A retroreflective ink containing microbeads as claimed in any one of Claims 18 to 21

23. An ink as claimed in Claim 22 including binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied.

24. An ink as claimed in Claim 23 including a coupling agent for coupling the microbeads and cross-linking the binder chemicals, the coupling agent being unreactive until the printing process is carried out.

25. A method for making a one-pack retroreflective ink comprising the steps of:

- making microbeads;
- suspending the microbeads in a liquid carrier medium;
- the liquid carrier medium comprising binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied and a coupling agent which couples the microbeads and cross-links the binder chemicals, the coupling agent being unreactive except at elevated temperature at which the printed substrate is cured.

26. A method according to Claim 25, comprising applying an aluminium coating to the microbeads.
27. A method according to Claim 26, comprising pre-treating the microbeads with stannous chloride prior to application of the aluminium coating.
28. A method according to Claim 27, in which the microbeads are treated with a dilute aqueous solution of stannous chloride.
29. A method according to any one of Claims 25 to 28, in which the microbeads are hemispherically metallised in a vacuum metallising process in which they are held on a film, optionally a polyester or polyolefin film, with an adhesive coating for transport through the metallising process, the adhesive coating comprising a styrene/butadiene type adhesive.
30. A method according to Claim 29 in which, following metallisation, the film is passed through an aqueous solution of citric acid.
31. A method according to Claims 29 or 30 in which the film is treated ultrasonically to assist in release of the microbeads from the adhesive surface.
32. A method according to any one of Claims 28 to 31 in which the microbeads are treated prior to inclusion in the ink with a silicate, optionally a dilute aqueous solution of sodium silicate.
33. A method according to any one of Claims 25 to 32 in which the microbeads are treated with a silane, preferably an amino silane, prior to inclusion in the ink.

34. A method according to Claim 32 or Claim 33 when dependent on Claim 29 in which the microbeads are treated with the silane, optionally an amino silane such as bis-[*gamma*-(trimethoxysilyl) propyl] amine, following the silicate treatment.

35. A method according to any one of Claims 25 to 34 in which an amino silanetriol, e.g. an amino silane, and/or a blocked polyisocyanate is added to the liquid carrier medium as coupling agent.

36. A method according to any one of Claims 25 to 35, in which a liquid carrier medium is prepared comprising binder chemicals and coupling agent, and the microbeads are added to the medium.

37. A method according to Claim 36, in which a further additive or additives are incorporated in the liquid carrier medium, said additives being selected from the group comprising:

pigment; humectant, optionally urea and/or 2,3 propane diol; buffer, optionally based on ammonium or sodium phosphates; dispersant; defoamer; thickening agent; cross-linking agent; softening agent; carbon black; UV absorbing material; anti-scuffing agent, optionally a silicone or fluoropolymer; light spill-suppressing agent; anti-static agent and water repellant agent, optionally a silicone or fluoropolymer.

38. A method according to Claim 37, in which a thickener is added to the liquid carrier medium in two steps, namely before and after the addition of the binder and coupler.

39. An ink produced by the method of any one of Claims 25 to 38.

40. A substrate coated or printed with ink as claimed in any one of Claims 14 to 17, 22 to 24 and 39.
41. A substrate as claimed in Claim 40 in the form of a screen for displaying projected images or a studio background for chroma-keying applications.
42. A substrate as claimed in Claim 40 in the form of flexible tape.
43. A method of providing a substrate with a retroreflective coating comprising applying to the substrate an ink as claimed in any one of Claims 14 to 17, 24 and 39, the ink having been formulated as a one-pack ink and the coupling agent being activated after the ink has been printed or coated on to the substrate.
44. A method as claimed in Claim 43 in which the coupling agent is activated by curing of the ink coating at elevated temperature.
45. A method as claimed in Claim 43 in which the coupling agent is activated by UV light or other high energy radiation during and/or after the printing process.
46. A retroreflective one-pack ink with a storage life of not less than 3 months, preferably not less than 6 months and more preferably not less than 12 months.
47. A retroreflective one-pack ink which has a viscosity of between 10 and 30 pascal after storage after storage for not less than 3 months, preferably not less than 6 months and more preferably not less than 12 months.
48. A retroreflective one-pack ink which has laundering durability such that retroreflectivity is not reduced by more than 40% (preferably by not more than 30%,

more preferably by not more than 20%) when applied to a substrate in the form of a cotton, nylon or polyester fabric and laundered for 5 cycles in accordance with ISO 6330, method 5A.

49. A fireproof or fire retardant fabric printed or coated with a retroreflective ink which comprises retroreflective elements in a polymeric matrix, the fabric comprising a structural component that chars before it melts.

50. A fabric according to claim 49 made fireproof or fire retardant by application of a fire retardant agent.

51. A fabric according to claim 50 in which the fire retardant agent comprises Proban ® or Pyrovatex ® or a like agent, applied to a cellulosic.

52. A fabric according to any one of Claims 49 to 52, the fabric comprising an aramid fibre.

53. A fabric according to any one of Claims 49 to 52, in which the ink is non-burning once applied to the fabric.

54. A fabric according to claim 53, in which the ink is aqueous-based and the polymeric matrix comprises polyvinylidene chloride.

55. A fabric according to claim 53, in which the polymeric matrix comprises polyvinyl chloride or other non-flammable plastisol.

56. A fabric as claimed in any one of Claims 49 to 55 in which the ink comprises an ink as claimed in any one of Claims 1 to 17, 22 to 24, 39 or 46 to 48.

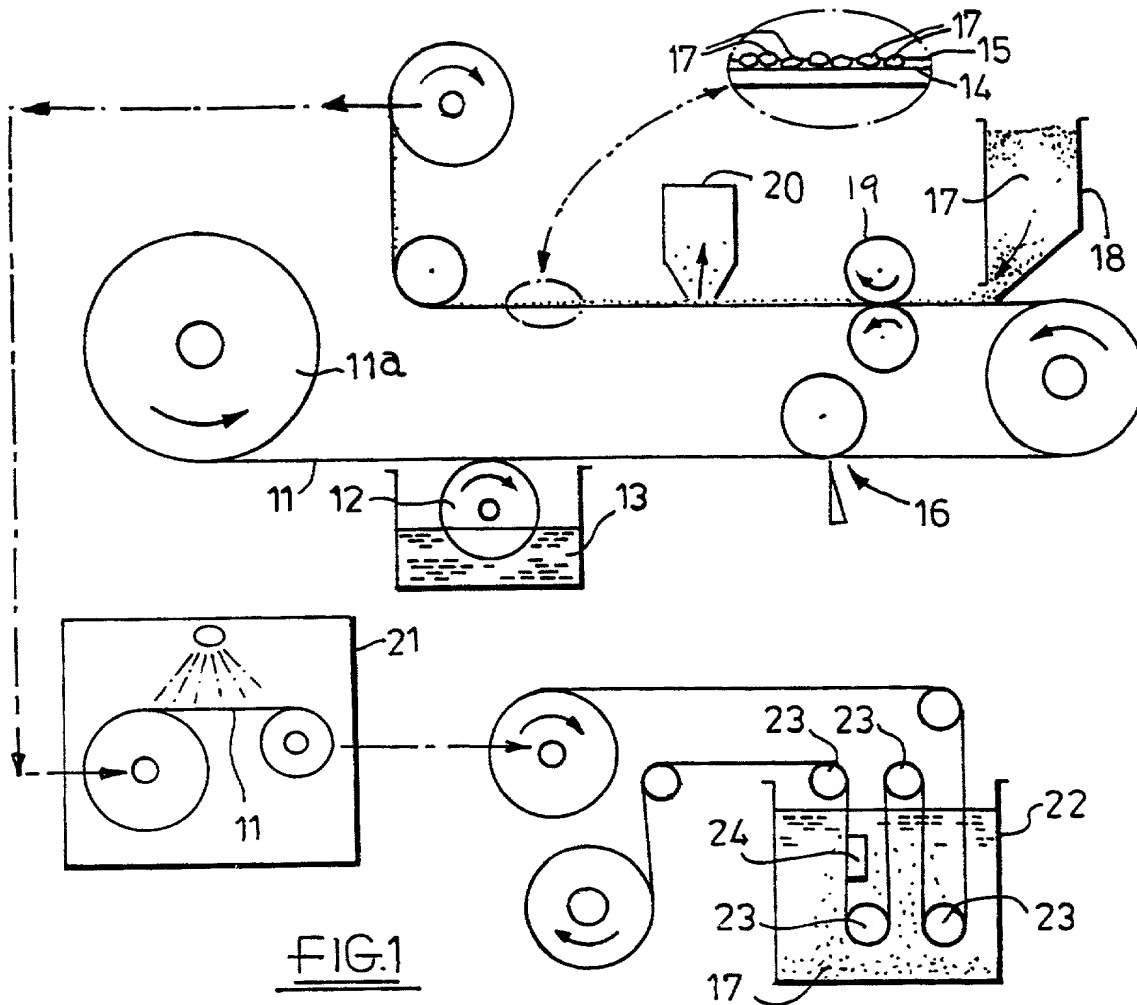


FIG. 1

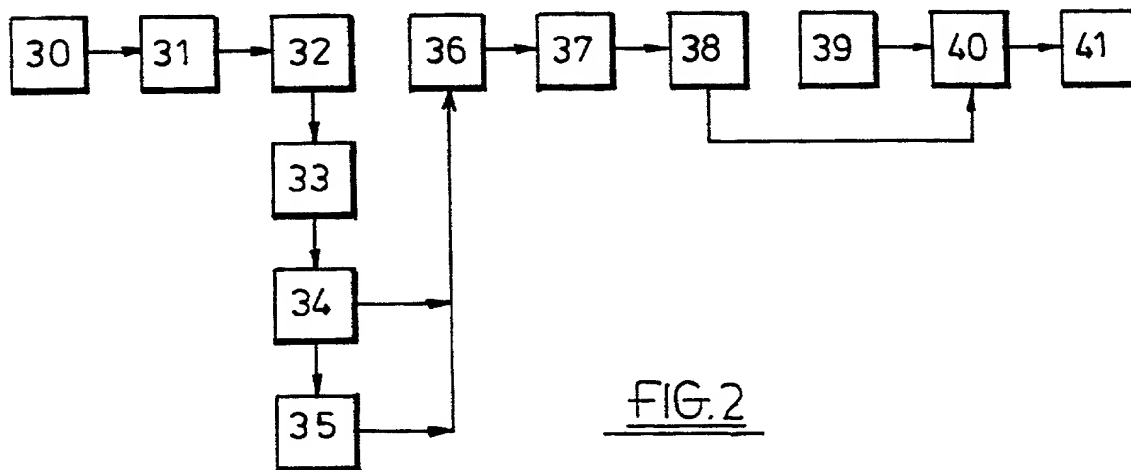


FIG. 2

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:]	§	DOCKET NO.: 069918.000002
Brian Sagar.	§	
	§	
SERIAL NO.: 09/889,282 ✓	§	GROUP ART NO.: Unknown
International: PCT/GB00/00062 ✓	§	
FILED:] 12 JAN 2000	§	
	§	EXAMINER: Unknown
TITLE: Retroreflective Inks	§	

DECLARATION

As below named inventor, I declare that:

My residence, post office address and citizenship are as stated below, next to my name,

I believe I am the original, first inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled **Retroreflective Inks** the specification of which

[ ] is attached hereto

☒ was filed on, 12 January 2000 ✓ as Application No. PCT/GB00/00062 ✓ and for which a preliminary amendment was filed in the USPTO on July 13, 2001 ✓

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:



Prior Foreign Application(s)

9900654.6	GB	Filed 14/01/99	Priority claimed: Yes
9901031.6	GB	Filed 19/01/99	Priority claimed: Yes
9921394.4	GB	Filed 10/09/99	Priority claimed: Yes
9921618.6	GB	Filed 14/09/99	Priority claimed: Yes

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

---

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s), or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

PCT Parent

12 January 2000

(PCT Filing date)

PCT/GB00/00062

(Application No.)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00 Full name of sole or first inventor: Brian Sagar

Inventor's Signature: Brian Sagar

Date: 1 September, 2001.

Residence

Citizenship: Great Britain

Post Office Address: The Cottage, 42 Moseley Road, Cheadle Hulme, Cheadle, Cheshire  
SK8 5HJ, GB CBX

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

Brian Sagar

SERIAL NO.: 09/889,282

FILED: July 13, 2001

TITLE: Retroreflective Inks

DOCKET NO.: 069918.000002

GROUP ART NO.: Unknown

EXAMINER: Unknown

POWER OF ATTORNEY

The Honorable Commissioner  
of Patents & Trademarks  
Washington, D.C. 20231

Sir:

The undersigned, being Assignee of the entire interest of the above-identified patent application by virtue of an assignment to be recorded in the U.S. Patent and Trademark Office, hereby elects, under 37 CFR §3.71, to prosecute this application to the exclusion of the inventor(s).

The Assignee hereby appoints:

James E. Bradley, Reg. No. 27,536;

Albert B. Kimball, Jr., Reg. No. 25,689;

Kent A. Rowald, Reg. No. 34,005;

Tim Cook, Reg. No. 32,561;

Shawn Hunter, Reg. No. 36,168;

Soumit Roy, Reg. No. 47,043;

Mark Tidwell, Reg. No. 37,456;

Bryan White, Reg. No. 45,211.

Robert C. Curfiss, Reg. No. 26,540;

Ben Tobor, Reg. No. 27,760;

Frank S. Vaden III, Reg. No. 22,236;

Jiewen C. Davis, Reg. No. 46,393;

Constance G. Rhebergen, Reg. No. 41,267;

Keith Taber, Reg. No. 46,114;

Darryl M. Tyus, Reg. No. 40,853, and

jointly and severally, as its attorney or agent, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to transact all business in the Patent and Trademark Office in connection therewith and to receive the Letters Patent. All previous powers, if any, are hereby revoked.

Please direct all communications to:

James E Bradley

Bracewell & Patterson, L.L.P.

P.O. Box 61389

Houston, Texas 77208-1389

(713) 223-2900

ASSIGNEE: **Reflec plc**

Signed:  \_\_\_\_\_

Name (CAPITALS): PETER WHITE

Title: DIRECTOR

Date: 18/07/01